INFLUENCE OF COMMON ION ON THE DISSOCIATION OF SOME STRONG ELECTROLYTES. PART I. SULPHURIC ACID AND BISULPHATES

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(Plate VI)

ABSTRACT. Influence of common ions on the dissociations of sulphuric acid and bisulphates is studied by taking the Raman spectra of the mixtures of these solutions with other acids which supply hydrogen ions and with normal sulphates which supply the sulphate ions. It was observed that while the addition of H ions suppressed the dissociation in all these cases, the addition of the sulphate ions to the bisulphate solutions helped further dissociation of the HSO_4 produced on dissolving the bisulphate in water. The latter result is in contradiction to the law of mass action.

INTRODUCTION

Interesting among the studies on the dissociation of strong electrolytes by Raman effect is the influence of common ion on the dossociation of an electrolyte suggested by Hibben (1937). He observed that a concentrated solution of $ZnCl_2$ gives a strong Raman line of frequency 275 which is characteristic of the undissociated $ZnCl_2$ molecules. As the solution is diluted, the line diminishes in intensity obviously due to the dissociation of $ZnCl_2$ molecules. But, when even to a comparatively dilute solution of $ZnCl_2$, NaCl is added, the line appears bright again. This was explained as arising out of the reforming of $ZnCl_2$ molecules due to the Cl ions which are supplied in abundance by the addition of NaCl. This is a natural consequence of the law of mass action. But, when he examined the influence of the kation, by adding $ZnSO_4$ the line did not increase in intensity. He explained the anomaly as due to the fact that in the latter mixture both $ZnCl_2$ and $ZnSo_4$ are homopolar. Similar investigations have been made by Venkateswaran (1935) on other halides which give Raman lines.

So far the experimental results, concerning the influence of common ion, are found to be in agreement with the law of mass action. But as the studies are extended to other strong electrolytes, to be dealt with in this series of investigations, they yield peculiar results which are difficult to understand, if one applies the law of mass action, even qualitatively. The present paper describes such investigations on sulphuric acid and bisulphates.

SULPHURIC ACID

In a previous paper (Rao, 1940) by the author, where a quantitative study of the dissociation of sulphuric acid in different concentrations was reported, it was observed that while the first stage of dissociation into H and HSO_4 ions is

rapid even in highly concentrated solutions, the further dissociation of HSO_4 into H and SO_4 is very slow, even in comparatively dilute solutions. This was explained as due to the large number H ions produced during the two stages, which therefore favours recombination of H and SO_4 ions into HSO_4 ions as expected from the law of mass action.

In the present work the dissociation of sulphuric acid, as influenced by the addition of H ions, is studied. HCl is a convenient acid for the supply of H ions because it is almost completely dissocrited even at high concentrations. But its addition to concentrated H_2SO_4 results in evolution of gaseous HCl. Hence it cannot be used for studying the drssociation characteristics of H_2SO_4 at high concentrations, though for dilute solutions of H_2SO_4 it is found to be very convenient. HNO_3 cannot be used as it gives a strong Raman line at 1050 which is superposed upon the 1045 line of H_2SO_4 corresponding to the HSO_4 ions, the intensity variation of which is taken as the basis for the study of the dissociation of this acid. Hence, $HClO_4$ was chosen as the source of supply of H ions for concentrated solutions of H_2SO_4. This acid, however, gives rise to a strong Raman line at 937 which is broad and falls very near the 910 line corresponding to the undissociated H_2SO_4 molecules. Thus the study of the variation of dissociation of H_2SO_4 with addition of $HClO_4$ is confined to the determination of the intensity of the 1045 line of the HSO_4 ion alone in the mixture and in the pure acid.

100 cc. of concentrated sulphuric acid 30N are taken and divided into two equal parts. To one part 30 cc. of 10N $HClO_4$ is added and to the other part 30 cc. of water. The Raman spectra of the two solutions exposed under identical conditions for equal times are taken, and the intensity of the 1045 line in the two spectra are determined and are found to be 17.3 and 7.0 in the pure acid and $HClO_4$ mixture, respectively. But the water content in the former solution is more than that in the mixture with $HClO_4$. So, the above comparison requires modification to one in which the water content is the same in both. If to the concentrated sample of H_2SO_4, only that amount of water as is contained in 30 cc. of $HClO_4$ (10N) is added, its normality will be reduced to 23N and the corresponding intensity of the 1045 line, calculated from the previous work of the author on dissociation of sulphuric acid with concentration, is 12.8. Therefore, it is clear that that the decrease in the intensity of the 1045 line is more than is warranted by the smaller amount of water in the mixture with $HClO_4$ compared to that with pure water and this should be attributed to the decrease in the dissociation of H_2SO_4 brought about by the H ions supplied by $HClO_4$.

To study the second stage of dissociation, 50 cc. of 3.6N sulphuric acid is taken and divided into two parts. To one part 25 cc. of concentrated HCl is added and to the other 25 cc. of water. It is clearly seen from the microphotometric curves *a* and *b* of the spectra given in Fig. 1 that the intensity of the line at 980 corresponding to the SO_4 ions is suppressed to a large extent thereby indicating that the dissociation of HSO is diminished in the HCl mixture. It would

have been interesting to see how the addition of the bisulphate ion influences the first stage of dissociation of the acid. But unfortunately, this is not practicable for the following reasons. Firstly, bisulphates dissolve but to a small extent in sulphuric acid at laboratory temperature. Secondly, even if it is possible to dissolve more at at a high temperature, the bisulphate ion contributes to a small extent to the intensity of the 910 line characteristic of undissociated H_2SO_4 molecules and therefore it is not possible to distinguish whether the changes in the intensity of the 910 line is due to the change in the dissociation of the acid or to that of the HSO_4 ions. Therefore, no attempt was made to test this.

ACID SULPHATES

It is well known that an alkaline bisulphate is completely dissociated as far as its alkaline radical is concerned and the Raman spectra of its solution which mainly consists of 4 lines at 1045, 980, 564 and 414 is therefore due to HSO_4 and SO_4 ions formed by the dissociation of HSO_4 ions. The line at 1045 is attributed by all workers to the HSO_4 ions, and that at 980 to SO_4 ions. The bands at 564 and 414 are characteristic of both the types of ions. As the solution is diluted, the line at 1045 diminishes in intensity, while that at 980 increases, thereby indicating dissociation of HSO_4 ions into SO_4 and H ions. The effect of the addition of H and SO_4 ions on the dissociation of HSO_4 in a solution of NH_4HSO_4 is studied in the following way .

A 3·4N solution of NH_4HSO_4 is taken and divided into two parts. To one part is added an equal volume of 10N HCl and to the other an equal volume of pure water. The Raman spectra of these two mixtures, exposed for equal times are taken under identical conditions. Their microphotometric curves are given in Figs. 2*a* and 2*b*. The spectra revealed that while the lines at 1045 and 980 are nearly of equal intensity in the water solution, in the mixture with HCl, the line at 980 is very much suppressed, which means that almost all the SO_4 ions recombined with H ions to form HSO_4 ions.

To study the influence of SO_4 ions on the dissociation of HSO_4 into SO_4 and H, the sample of the solution of NH_4HSO_4 is taken and divided into two equal parts. To one part is added solid $(NH_4)_2SO_4$, to saturation. This resulted in an increase of volume of the solution. To the other part is added pure water to make up to this volume. Raman spectra of the two mixtures exposed for equal times under identical conditions are taken. Since the 980 line in the spectrum of the sulphate mixture is due to the SO_4 ions supplied by the bisulphate as well as the sulphate, the intensity of the 1045 line only representative of the HSO_4 ion is compared in the two solutions. It is seen from the Fig. 3*b* and 3*a* in Plate VI that the line at 1045 is more intense in the pure bisulphate solution than in the mixture with normal sulphate. This means that the addition of the normal sulphate favours further dissociation of the HSO_4. This result is confirmed in the mixtures of $KHSO_4 + (NH_4)_2SO_4$ and $NH_4HSO_4 + Li_2SO_4$ also.

In this connection, one point requires elucidation. In the case of the mixtures with HCl, the mixture and pure solution contain very nearly the same proportion of water. But in the case of the solutions of pure acid sulphate and the mixtures of acid sulphate and normal sulphate, the latter contain less amount of water and still the dissociation of HSO_4 is more in these mixtures than in the corresponding pure solutions. It means, that the increase of dissociation brought about by the additional SO_4 ions more than compensates the opposite effect caused by the decrease in the proportion of water. This is contrary to what is to be expected from the law of mass action.

The possibility of complications arising out of the reaction $SO_4 + H_2O \rightleftharpoons HSO_4 + OH$ is excluded, because Raman spectra of solutions of normal sulphates even after long exposures do not indicate even traces of the line 1045 corresponding to the HSO_4 ions.

TO SUM UP

1. The dissociation of sulphuric acid is decreased by the addition of other electrolytes which supply H ions in abundance namely HCl and $HClO_4$ worked with in the present case.

2. The dissociation of HSO_4 into SO_4 and H is suppressed by the addition of electrolytes which supply H ions, *e.g.*, HCl used in the present case.

3. The dissociation of HSO_4 into SO_4 and H is enhanced by the addition of SO_4 ions supplied by a normal sulphate.

It is well known that the law of mass action is applicable only to very dilute solutions of weak electrolytes. For concentrated solutions, the constant is found to vary with concentration involving the formation of less number of undissociated molecules. But a case of enhancement of dissociation by the addition of one of the dissociated products is not contemplated before. Another point of interest is the discrimination between the ions involving an extreme case of inapplicability of the above law which was also not contemplated before.

Further work on the point is in progress to permit of a generalisation as regards the dissociation characteristics of strong electrolytes having an ion common to them.

In conclusion, the author takes great pleasure in recording his grateful thanks to Dr. I. Ramakrishna Rao, under whose direction this work was done.

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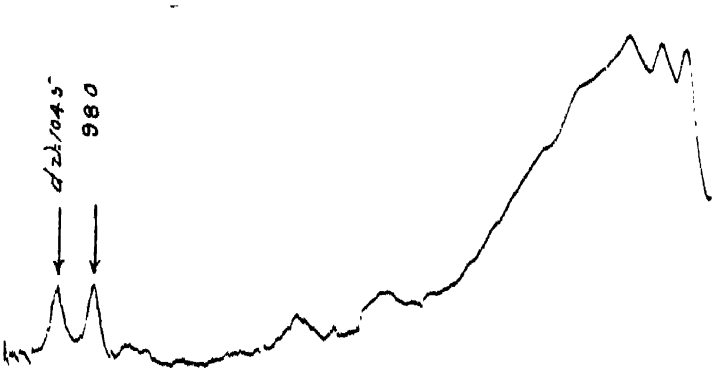
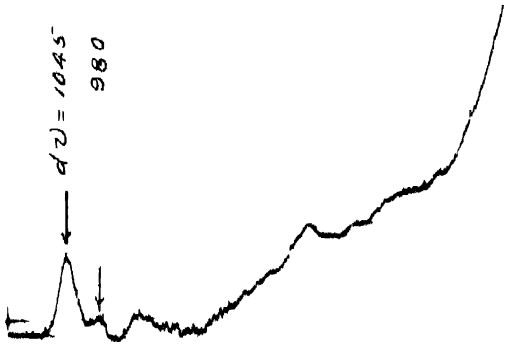
PLATE VI (A)



H_2SO_4 pure



H_2SO_4 + Hel

Fig. 1
Sulphuric Acid and Bisulphate

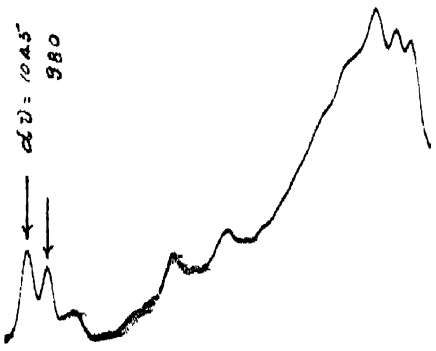


Fig. NH_4HSO_4 pure

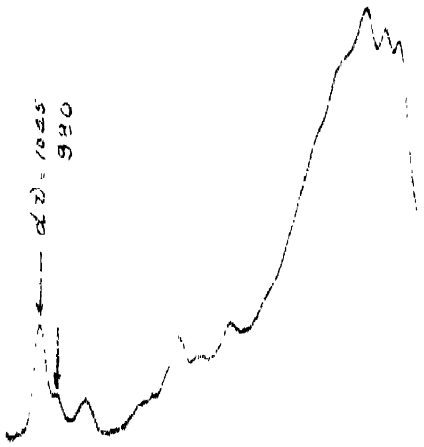
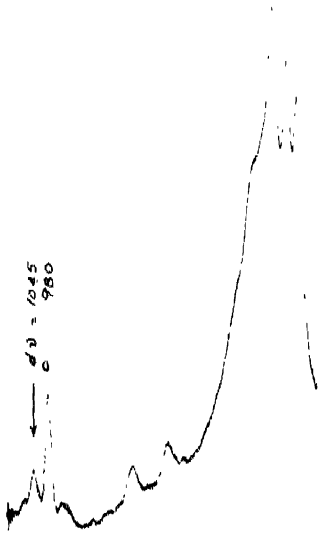
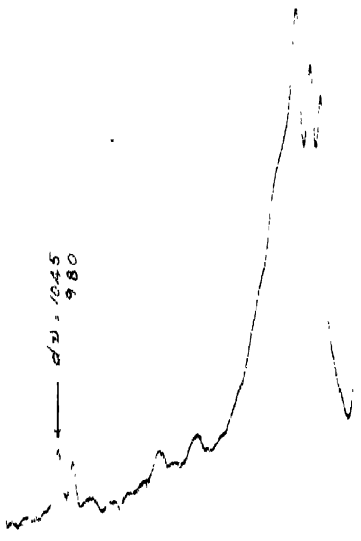


Fig. 2b — NH_4HSO_4 + HCl



NH_4HSO_4 + $(NH_4)_2SO_4$

Fig. 3.



NH_4HSO_4